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Patentanmeldung Nr. Patent application No. Demande de brevet n°

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Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
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TITLE

POROUS MATERIAL, METHOD AND ARRANGEMENT FOR CATALYTIC CONVERSION OF EXHAUST GASES

TECHNICAL FIELD

The invention refers to a porous material for catalytic conversion of exhaust gases. Said porous material comprises a carrier with a first porous structure, and an oxidation catalyst which in the presence of oxygen, according to a first reaction, has the ability to catalyse oxidation of nitrogen monoxide into nitrogen dioxide and, according to a second reaction, to catalyse oxidation of a reducing agent, which oxidation catalyst is enclosed inside the first porous structure.

Preferably, the porous material also comprises a carrier with a second porous structure and a reduction catalyst, which in the presence of the reducing agent is able to further catalyse reduction of nitrogen dioxide into nitrogen, whereby the reducing agent is at least partially consumed. The invention also relates to a method and an arrangement and a catalytic conversion device which utilise the porous material, and indicates an advantageous use of the porous material.

The invention may be applied within the field of catalytic conversion of exhaust gases which originate from internal combustion engines, particularly Lean Combustion engines (LC-engines) and diesel engines.

The present invention may also be utilised for other exhaust gases, containing nitrogen oxides and having an oxygen surplus, which originate from stationary emission sources such as gas turbines, power plants and the like.

BACKGROUND ART

When attempting to reduce the emissions of nitrogen oxides (NO_x) from internal combustion engines, a lot of efforts have been made to modify the combustion conditions in order to reduce the NO_x-emissions, while still maintaining the combustion efficiency at a satisfactory level.

Amongst the traditional techniques for the reduction of NOx-emissions may, inter alia, the technique of Exhaust Gas Recirculation (EGR) be mentioned, as well as special designs of fuel injectors and combustion chambers. Other important parameters are compression, fuel injection time and fuel injection pressure. Techniques involving water injection, the use of fuel/water emulsions and so-called Selective Catalytic Reduction (SCR) by ammonia, have also been employed. Thereby, it has been found that a one-sided optimisation of the combustion efficiency often results in increased NO_x-emissions.

Today, it is required that both the fuel consumption and the NO_x-emissions are reduced. There are also strong demands on reduced emissions of other chemical compounds which are potentially hazardous to the environment, e.g. hydrocarbons.

Accordingly, there is an increased need for catalytic converters which also are able to treat exhaust gases from so-called Lean Combustion (LC) engines. Therefore, a number of different catalytic converters have been developed and are well-known from commercial applications in e.g. motor vehicles.

Typically, conventional catalytic converters comprise one or several matrices, or monolith bricks as they sometimes are called. Such bricks or monoliths are in the form of a ceramic honeycomb substrate, with through passages or cells, and can be furnished with a porous surface coating. Particles of a suitable catalyst are embedded in the surface of the matrix, and the design of the matrix has been optimised in order to maximise the surface area over which catalytic reactions take place. Common catalysts are noble metals, e.g. silver (Ag), platinum (Pt), palladium (Pd), rhodium (Rh), gallium (Ga) or ruthenium (Ru) or mixtures of these. There are also a number of other metals and metal oxides which may be used as catalysts. Such catalysts may have the ability to catalyse oxidation or reduction reactions, or both.

It is also previously known to use crystalline aluminium silicates, so-called zeolites, loaded with a suitable catalyst. The use of zeolites in connection with the catalytic conversion of exhaust gases is disclosed in e.g. EP 0 499 931 A1 and EP 0 445 408 A.

Furthermore, it is also previously known to combine several different catalytic matrices, or to arrange a so-called after-burner in the catalytic conversion process. Such arrangements are disclosed in e.g. U.S. Patent No. 5,465,574.

It is also previously known to use a honeycomb monolith of corrugated metal foil coated with a suitable catalytic material carried or supported on its surface.

It has also been suggested, e.g. in EP 0 483 708 A1, to combine a conventional ceramic catalytic converter with an electrically heat-able catalytic converter in order to ensure that the optimum temperature for catalytic conversion is maintained.

Thus, a number of different catalyst materials, devices, and arrangements for the catalytic conversion of exhaust gases have been described in the art.

Thereby, it is believed that simultaneous elimination of nitrogen oxides (NO_x) and hydrocarbons (H_xC_y) may take place over e.g. an Ag-catalyst, according to the (simplified) chemical reactions:

A) $NO_x + H_xC_y \rightarrow N_2 + H_2O + CO_2 + CO$

and

B) $O_2 + H_xC_y \rightarrow H_2O + CO_2$

However, in practice, it has been found that the following reaction is predominant:

C) $$NO_2 + H_xC_y \rightarrow N_2 + H_2O + CO_2$$

It should be noted that the term H_xC_y in the chemical reactions herein not only refers to hydrocarbons but is also relevant for other reducing agents which further comprise oxygen and/or sulphur. Accordingly, the reducing agent H_xC_y could also be expressed as $H_xC_yO_zS_w$. Examples of reducing agents which might be present in exhaust gases are alkanes, alkenes, paraffines, alcohols, aldehydes, ketones, ethers or esters and different sulphur-containing compounds. Also CO or H_2 could act as reducing agents. The reducing agent in the exhaust gases can originate from the fuel or the combustion air, or it can be added to the exhaust gases on purpose.

It has earlier been found that the above-mentioned reaction according to C) is very rapid over e.g. Ag-catalysts. Acidic catalysts (H^+) and acidic zeolites, doped with Ag or other suitable catalysts, have been found to be selective in the sense that NO_2 will readily be converted, whereas NO will not. This can be a great disadvantage since NO is predominant in "lean" exhaust gases from e.g. LC-engines. Another problem is that the available amount of NO_2 can become limiting for the reduction of hydrocarbons (H_xC_y) or other undesired compounds. The doping of zeolites with silver (Ag) or other metals such as iron (Fe) is disclosed in e.g. EP 0955080, and EP 0406474 discloses low silica MFI as a good basic structure for use in the mentioned applications.

In order to solve this problem, i.e. to be able to reduce the amount of both NO and H_xC_y in the exhaust gases, it has earlier been suggested to combine an Ag-zeolite catalyst with a Pt-catalyst.

Normally, the following main reactions will take place over a conventional Pt-catalyst:

D) $NO + 1/2\ O_2 \rightarrow NO_2$

E) $O_2 + H_xC_y \rightarrow H_2O + CO_2$

F) $2\ NO + H_xC_y \rightarrow N_2O + H_2O + CO_2$

When using a conventional Ag-zeolite catalyst in combination with a conventional Pt-catalyst, all four reactions C), D), E) and F) will occur. However, since hydrocarbon (H_xC_y) is consumed in the chemical reactions E) and F), there is a risk that there will not be a sufficient amount of hydrocarbon (H_xC_y) left for the reaction with nitrogen dioxide (NO_2), according to reaction C). This results in an undesired residue of nitrogen dioxide (NO_2) in the catalytically converted exhaust gases, originating from reaction D).

Previous attempts have been made to solve this problem with different types of catalysts, by means of combining different catalysts, and by means of adding an additional amount of hydrocarbon to the exhaust gases in order to supply the reaction C) with a sufficient amount of hydrocarbon.

However, many of the previous solutions have been associated with the problem of undesired oxidation of hydrocarbons (H_xC_y) over at least some surfaces of the oxidation catalyst, which preferably only should catalyse oxidation of nitrogen monoxide (NO) into nitrogen dioxide (NO_2), according to reaction D).

Another problem associated with many previously known catalysts is that, during certain conditions, they will catalyse reaction F) which produces dinitrogen oxide (N_2O). This reaction is undesired and it is preferred that the nitrogen oxides (NO_x) in the exhaust gases are converted into nitrogen (N_2) to the highest possible degree, and not into dinitrogen oxide (N_2O).

In WO 99/29400 it has been proposed to solve this problem by providing a porous material for catalytic conversion of exhaust gases, by means of which porous material it is possible to selectively catalyse the oxidation of nitrogen monoxide (NO) into nitrogen dioxide (NO_2) and avoid catalytic oxidation of hydrocarbons (H_xC_y) or other reducing agents.

This is achieved by means of a porous material for catalytic conversion of exhaust gases which comprises a carrier with a first porous structure, and an oxidation catalyst. In the presence of oxygen, the oxidation catalyst has the ability to catalyse oxidation of nitrogen monoxide into nitrogen dioxide, according to a first reaction. Furthermore, the oxidation catalyst in itself has the ability to catalyse oxidation of a reducing agent, according to a second reaction. According to WO 99/29400, the oxidation catalyst is enclosed inside the porous structure, which first porous structure has pores with such dimensions that the reducing agent is sterically prevented from coming into contact with the oxidation catalyst. This will enable primarily the first reaction, out of said first and second reactions, to take place over the oxidation catalyst during the catalytic conversion of the exhaust gases.

According to WO 99/29400, the catalyst further comprises a reduction catalyst enclosed in a second porous structure, which second porous structure has pores with greater dimensions than the pores in the first porous structure, enabling the reducing agent to react with the nitrogen dioxide (NO_2) according to a third reaction.

Using the described porous structures of two different sizes as described above is an improvement of a selective catalytic reaction, but there is still need for even better applications and methods for catalytic conversion of exhaust gases. For example, the porous material described uses strong oxidation agents, preferably such as platinum (Pt) and/or Palladium (Pd), and this puts high demands on the production. It is important that the strong oxidation agent does

not contaminate the outside of the oxidation pore, since such a contamination would oxidate and consume some of the H_xC_y, thereby diminishing the reducing agent necessary for reducing NO_2 to N_2 according to the favourable reaction third reaction.

TECHNICAL PROBLEM:

Accordingly, there is a need for an improved, selective oxidation catalyst material, which catalyses oxidation of nitrogen monoxide (NO) into nitrogen dioxide (NO_2) and which does not catalyse oxidation of hydrocarbons.

Furthermore, there is also a need for an effective combination of such a selective oxidation catalyst material, catalysing a reaction which produces nitrogen dioxide (NO_2), and a reduction catalyst material, catalysing a reaction in which nitrogen dioxide (NO_2) is reduced by hydrocarbons or other reducing agents into nitrogen (N_2).

DISCLOSURE OF THE INVENTION:

Accordingly, a first object of the present invention is to provide a porous material for catalytic conversion of exhaust gases, by means of which porous material it is possible to selectively catalyse the oxidation of nitrogen monoxide (NO) into nitrogen dioxide (NO_2), and avoid catalytic oxidation of hydrocarbons (H_xC_y) or other reducing agents.

This first object of the invention is achieved by means of a porous material for catalytic conversion of exhaust gases which, according to claim 1, comprises a carrier with a first porous structure, and an oxidation catalyst. In the presence of oxygen, the oxidation catalyst has the ability to catalyse oxidation of nitrogen monoxide into nitrogen dioxide, according to a first reaction. Furthermore, the oxidation catalyst in itself has the ability to catalyse oxidation of a reducing agent, according to a second reaction. According to the invention, the oxidation catalyst is enclosed inside the porous structure, which due to the presence of the catalytically active iron and silver prevents the reducing agent from reacting

in the oxidation catalyst or slows down the reaction of the reducing agent in the oxidation catalyst. This will enable primarily the first reaction, out of said first and second reactions, to take place over the oxidation catalyst during the catalytic conversion of the exhaust gases.

According to one embodiment of the invention the oxidation catalyst comprises iron and silver loaded on a zeolite, and the first porous structure may comprise a zeolite with MFI framework structure type.

Furthermore, a second object of the present invention is to provide a porous material for catalytic conversion of exhaust gases, wherein primarily only the desired reactions take place, as a result of which the contents of NO, NO_2 and H_xC_y in the catalytically converted exhaust gases are effectively decreased, and the resulting conversion products primarily are nitrogen (N_2), carbondioxide (CO_2) and water (H_2O), and not dinitrogen oxide (N_2O).

The second object of the invention is achieved by means of a porous material according to claim 1 which, in accordance with claim 3, further comprises a carrier with a second porous structure and a reduction catalyst. In the presence of a reducing agent, the reduction catalyst is able to selectively catalyse reduction of nitrogen dioxide into nitrogen, according to a third reaction, whereby the reducing agent participates in the third reaction and is at least partially consumed. Thereby, the reduction catalyst is located in the second porous structure, which has such dimensions that the reducing agent can come into contact with the reduction catalyst in order to enable the third reaction to take place.

A third object of the present invention is to provide a method for catalytic conversion of exhaust gases in which the porous material according to the invention is utilized.

The third object of the invention is achieved by means of a method for catalytic conversion of exhaust gases which, according to claim 22, comprises oxidation of nitrogen monoxide into nitrogen dioxide over an oxidation catalyst, according to a first reaction, whereby said oxidation catalyst also has the ability to, according to a second reaction, catalyse oxidation of a reducing agent. According to the invention, however, the reducing agent is prevented from coming into contact with the oxidation catalyst or that the reaction of the reducing agent in the oxidation catalyst is slowed down, as a result of which primarily the first reaction, out of said first and second reactions, takes place over the oxidation catalyst, due to the presence of iron and silver, as a result of which primarily the first reaction, out of said first and second reactions, takes place over the oxidation catalyst.

A fourth object of the present invention is to indicate an advantageous use of the porous material according to the invention.

In accordance with the invention, the fourth object is achieved by the use of a porous material according to the invention, providing functions both for the oxidation of nitrogen monoxide into nitrogen dioxide and for the reduction of nitrogen dioxide into nitrogen, for catalytic conversion of exhaust gases which have an oxygen surplus.

Finally, a fifth object of the present invention is to provide an advantageous arrangement for catalytic conversion of exhaust gases, utilizing the porous material according to the invention.

In accordance with the invention, the fifth object of the invention is achieved by an arrangement, for catalytic conversion of exhaust gases from an internal combustion engine, comprising a porous material according to the invention.

Furthermore, according to the invention a catalytic conversion device for exhaust gases comprises a porous material according to invention.

The respective first reaction, the second reaction and the third reaction mentioned above may not be only one separate reaction step, but may also be a series of reaction steps.

BRIEF DESCRIPTION OF DRAWINGS

In the following, the invention will be described in greater detail with reference to the attached drawings and graphs.

Fig. 1 shows a schematic view of a portion of a porous material according to the invention, also with an enlarged view seen from inside a pore in the porous material. The major chemical reactions which occur during the catalytic conversion of exhaust gases are also indicated.

Fig. 2 schematically depicts an embodiment of the porous material according to the invention, with an enlarged detailed view of a portion of the porous material including a supporting substrate.

Fig. 3A schematically shows an enlarged detailed view of a portion of the enlarged detailed view in Fig. 2, and depicts a variant of the porous material according to the invention, comprising a physical mixture of two different zeolite carriers.

Fig. 3B schematically shows another enlarged detailed view of a portion of the enlarged detailed view in Fig. 2, and depicts another variant of the porous material according to the invention, comprising a layered structure of two different zeolite carriers.

Fig. 3C schematically shows an alternative to the layered structure in Fig. 3B.

Fig. 4A schematically shows an embodiment of a porous material according to the invention, having a first portion and a second portion.

Fig. 4B schematically shows another embodiment of the invention, wherein the porous material according to the invention comprises two separate, different parts, intended to be used together in a single catalytic conversion process.

Fig. 5 shows a schematic process diagram of an arrangement for catalytic conversion of exhaust gases according to the invention.

MODES FOR CARRYING OUT THE INVENTION

In the following, a porous material according to the invention will be described with reference to the attached drawings.

The porous material 1 in Fig. 1 comprises a carrier with a first porous structure 2, 2'. An oxidation catalyst (OX) is enclosed inside the first porous structure 2, 2'. In the presence of oxygen (O_2), the oxidation catalyst (OX) has the ability to catalyse oxidation of nitrogen monoxide (NO) into nitrogen dioxide (NO_2), according to a first reaction 3. Furthermore, the oxidation catalyst (OX) in itself has the ability to catalyse oxidation of a reducing agent (HC), according to a second reaction 4, 4' (indicated with 4, 4' in Fig. 1).

According to the invention, however, such oxidation of the reducing agent according to the second reaction 4, 4' is not desired, since the reducing agent (HC) is more useful in a third reaction, as will become apparent below.

In order to prevent the undesired second reaction 4, 4' from occurring, the oxidation catalyst (OX) is enclosed inside the first porous structure 2, 2', and the oxidation catalyst (OX) comprises iron (Fe) and silver (Ag) loaded on a zeolite, Due to the iron (Fe) and silver (Ag) in the oxidation catalyst (OX) in the first porous structure 2, 2', the reducing agent (HC) is prevented from reacting in the oxidation catalyst (OX), or the reaction of the reducing agent (HC) in the oxidation catalyst (OX) is at least slowed down. This will enable primarily the

desired first reaction 3, out of said first and second reactions, to take place over the oxidation catalyst (OX) during the catalytic conversion of exhaust gases. In this context, the term "first porous structure" primarily refers to internal micro-pores in the carrier material or micro-pores between carrier particles or grains. The first porous structure (2, 2') may advantageously comprise a zeolite with MFI framework structure type.

Preferably the first porous structure (2, 2') comprises a silica oxide structure where the oxidation catalyst (OX) comprises iron (Fe) and silver (Ag). The presence of both iron (Fe) and silver (Ag) has proven to be advantageous in many aspects. One advantage is that iron (Fe) and silver (Ag) are not as strong oxidation agents as e.g. platinum, Pt, which is an advantage in that even if some iron (Fe) and/or silver (Ag) has landed upon the outside of the oxidation catalyst (OX), only a small part of the reducing agent (HC) is oxidated. The use of iron (Fe) and silver (Ag) in combination in an oxidation catalyst (OX) according to the invention, has empirically proven to give a surprisingly high conversion of NO_x into N_2 and hydrocarbons into carbon dioxide and water, compared to previously known oxidation catalysts consisting of for example, platinum, rhodium, or silver.

As mentioned before it is previously known to use iron in combination with materials with strong catalytic features, e.g. platinum, and it is also known to use silver in combination with materials with strong catalytic features, e.g. platinum. But, since both iron and silver are relatively weak catalyst materials it has not previously been suggested to combine iron and silver according to the invention in order to get a high conversion of NO_x into N_2 . On the contrary, all previously known catalysts use at least one strong catalyst material in order to gain sufficient conversion of NO_x into N_2. Thus, the use of the combination of the relatively weak catalyst materials iron and silver, without any strong catalyst material, has, as mentioned before, shown surprisingly high conversion features of NO_x into N_2, i.e. using two relatively weak catalyst materials such as iron and silver is not the natural choice to make when wanting to enhance the

rate of conversion of NO_x into N_2 , but the more natural choice would be to elaborate with stronger catalytic materials. But the use of a stronger catalytic material enhances the risk of consuming the reducing agent (HC) by oxidation, thereby diminishing the amount of reducing agent (HC).

Preferably, the porous material 1 further comprises a carrier with a second porous structure 5, 5', in which a reduction catalyst (RED) is located. In this context, the term "second porous structure" can include internal micro-pores in the carrier material, or cavities or channels between carrier particles, but also cavities inside or channels through the porous material, i.e. macro-pores. In the presence of a reducing agent (HC), the reduction catalyst (RED) is able to selectively catalyse reduction of nitrogen dioxide (NO_2) into nitrogen (N_2), according to a third reaction 6, shown schematically i Fig. 1. Thereby, the reducing agent (HC) participates in the third reaction 6 and is at least partially consumed.

According to the invention, the reduction catalyst (RED) is located in the second porous structure 5, 5', which has such dimensions that the reducing agent (HC) can come into contact with the reduction catalyst (RED). This enables the desired third reaction 6 to take place during the catalytic conversion of exhaust gases.

According to one embodiment of the porous material, both the first 2, 2' and the second 5, 5' porous structures are provided in the same layer or coating of the porous material.

If desired, however, the first 2, 2' and the second 5, 5' porous structures can be provided in different layers/coatings of the porous material. This might be an advantage, depending on the composition of the exhaust gases which are to be catalytically converted.

In one embodiment of the porous material, the carrier with the second porous structure 5, 5' is adapted to the molecule size and/or the adsorption properties of the reducing agent (HC) or agents, which is/are expected to occur in the exhaust gases.

In another embodiment of the porous material, the ratio between the oxidation catalyst (OX) and the reduction catalyst (RED) has been optimized so that the production of nitrogen dioxide (NO_2), according to the first reaction 3, essentially corresponds to the consumption of nitrogen dioxide (NO_2), according to the third reaction 6.

In still another embodiment of the invention (Fig. 4A), the porous material further comprises a first portion 10 and a second portion 11, wherein the first portion 10 is intended to receive exhaust gases 12 before the second portion 11 during the catalytic conversion. Thereby, the first portion 10 contains a larger quantity of the oxidation catalyst (OX) than the second portion 11, whereas the second portion 11 contains a larger quantity of the reduction catalyst (RED) than the first portion 10. Accordingly, in a flow of exhaust gases the first reaction 3, producing NO_2, will take place upstream the third reaction 6, which consumes NO_2. As shown in Fig. 4B, It is also conceivable with embodiments wherein the first and second portions are separated from each other, as long as they used for catalytic conversion in the same conversion process. Thus, a catalytic conversion device for exhaust gases comprises a porous material according to invention. For example, the catalytic conversion device comprises a first- and a second portion 10,11 according to the above,

According to one embodiment of the porous material, the first 2, 2' and/or the second 5, 5' porous structure is provided in a carrier which is a zeolite crystal structure.

Furthermore, both the first 2, 2' and the second 5,5' porous structures can be provided in carriers of zeolite type, wherein preferably the first porous structure

2, 2' is provided in a first zeolite 14 and the second porous structure in a second zeolite 15.

As earlier mentioned, according to the invention, the first porous structure 2, 2' and, accordingly, also the first zeolite 14 should provide suitable properties in order to prevent the earlier-mentioned, undesired second reaction from taking place.

There are a number of different ways of combining different zeolites in a porous material according to the invention. Accordingly, the porous material can comprise a physical mixture 13 of the first zeolite 14 and the second zeolite 15 (Fig. 3A).

Furthermore, the porous material can comprise a layered structure 16, 17 of the first zeolite and the second zeolite (Figs. 3B and 3C). Different layers may also be applied or coated onto different supporting substrates 18 or different surfaces of a substrate 18.

In certain applications, it may be preferred to arrange the layered structure 17 so that, in a flow of exhaust gases, the second zeolite will encounter the exhaust gases before the first zeolite. This might be the case e.g. when the exhaust gases which are to be converted contain a proportionately high content of NO_2 but a low content of NO.

In other applications, e.g. when the content of NO in the exhaust gases is proportionately high but the content of NO_2 is low, it might be desirable to arrange the layered structure 16 in the opposite way, i.e. the first zeolite outside the second zeolite.

According to one embodiment of the porous material, a layered structure is achieved by means of the second zeolite 15, which provides the second porous

structure 5, 5', being crystallised onto the first zeolite 14, which provides the first porous structure 2, 2'. This can be done by means of so-called over-growth.

Another embodiment of the porous material aims at further reducing the occurrence of the earlier-mentioned, undesired second reaction. In this embodiment, the content of oxidation catalyst (OX) has been reduced in the outer layers 8 of the first zeolite by means of partial ion exchange (indicated in Fig. 1). Methods for altering the penetration depth and dispersion of the catalytically active metals are well known to the skilled person and will not be described in any greater detail.

In another embodiment of the porous material, an additional zeolite crystal layer with a reduced content of oxidation catalyst (OX) has been crystallized onto the first zeolite, by means of so-called over-growth. Thereby, the additional layer advantageously comprises a zeolite which provides a porous structure with smaller pores/entrances than the first zeolite. In this way, undesired reducing agent can more effectively be prevented from getting inside the internal pore structure of the first zeolite, at the same time as the nitrogen oxide (NO) will be admitted and can move freely inside said internal pore structure.

Also the dimensions of the crystal grains in the zeolite crystal structures can be used in order to facilitate desired chemical reactions, and in order to prevent undesired chemical reactions. Different crystal structures can be achieved in several different ways, e.g. by means of the choice of the crystallisation conditions and the choice of zeolite type. Also the internal pore structure of the zeolites is influenced by the choice of zeolite type.

Thus, according to one embodiment of the porous material, the size 9 and shape of the crystal grains in the crystal structure of the first zeolite, has been optimised both in order to prevent reaction of the reducing agent (HC), and in order to allow oxidation of NO to NO_2. The optimisation of the grain size is

important since it makes it possible to maximise the oxidation of NO into NO_2, and to minimise the oxidation of HC.

In another embodiment of the porous material, a proportionately small pore size, in the crystal structure of the first zeolite which provides the first porous structure 2, 2', has been achieved by means of selecting a zeolite with MFI framework Type (Framework types are listed in the Atlas of Zeolite Framework Types, available on the internet: www. iza-online.org). This zeolite is loaded with iron and silver to reduce the reaction of the reducing agent (HC).

As earlier mentioned, the porous material according to the invention has the ability to catalyse oxidisation of nitrogen monoxide (NO) into nitrogen dioxide (NO_2), and preferably also the ability to selectively catalyse reduction of nitrogen dioxide (NO_2) into nitrogen (N_2) in the presence of a reducing agent (HC). Thereby, the reducing agent (HC) may be any suitable reducing agent which is present in, or added to, the exhaust gases which are to be catalytically converted.

It is an advantage, however, if the reducing agent (HC) in the exhaust gases is a hydrocarbon (H_xC_y) or a chemical compound comprising oxygen and sulphur ($H_xC_yO_zS_w$). These compounds can originate from the fuel which is combusted and will, as earlier mentioned, be at least partially consumed according to the earlier-mentioned third reaction 6 over the reduction catalyst (RED). Alternative fuels, e.g. rape methyl ether, may produce oxygen-containing compounds, whereas sulphur is frequently present in most fuels.

The reduction catalyst (RED) in the second porous structure 5, 5' might be of any suitable, previously known type. However, in the porous material according to the invention, the reduction catalyst (RED) preferably comprises Brönstedt acid sites, silver (Ag), Iron (Fe), copper (Cu), Rhodium (Rh), Cobalt (Co), Indium (In), Iridium (Ir) or combinations of these. In the porous material

according to the invention, acidic zeolite catalysts are preferred as reduction catalysts (RED).

The herein used term "porous material" should be regarded as including the entire structure/mass which might be present inside a unit for the catalytic conversion of exhaust gases. Accordingly, the term "porous" should be understood both in a microscopic and in a macroscopic sense, i.e. the porous material could comprise elements which in them selves are not porous to exhaust gases. However, the material structure as a whole, i.e. the "porous material" according to the invention, will allow the exhaust gases which are to be catalytically converted to pass through. It should also be noted that embodiments wherein the porous material is composed of several separated parts, having different structures and functions, are conceivable, as long as they are used in the same catalytic conversion process.

The porous material, according to the invention, may be coated onto one or several suitable substrates 18 or matrixes in order to provide a carrier or several carriers which comprise the first or/and the second porous structures. Suitable substrates for this purpose are well known from the prior art, and will not be described in any greater detail, especially since they are of minor importance for the invention.

Accordingly, the substrate 18 may be a metal substrate of a previously known type. The substrate 18 may also be a supporting, previously known, honeycomb structure of a suitable material, with or without catalytic activity.

It should also be noted that the term "porous structure" used herein should be understood as to include both micro-pores and macro-pores of the porous material. Accordingly, internal micro-pores, cavities between carrier particles, channels inside or through the porous material, etc., are all included within the scope of "porous structure".

According to one embodiment of the invention, the method further comprises reduction of nitrogen dioxide (NO_2) into nitrogen (N_2) over a reduction catalyst (RED) in the presence of a reducing agent (HC), according to a third reaction 6. Thereby, the reducing agent (HC) participates in the third reaction 6 and is at least partially consumed. In this way, catalytically converted exhaust gases 12' (Fig. 5), having a reduced content of nitrogen monoxide (NO), nitrogen dioxide (NO_2) and reducing agent (HC) and a proportionately low content of dinitrogen oxide (N_2O), are obtained. Furthermore, the converted exhaust gases will have a reduced content of carbon monoxide (CO).

When desirable, an additional amount 19, 19', 19" of reducing agent (HC) can be added with a suitable injection device 28, before reduction takes place over the reduction catalyst (RED), according to the third reaction 6 (Figs. 1 and 5). In this way, the stoichiometrics of the occurring chemical reactions can be influenced so that the catalytic conversion becomes as complete as possible. In internal combustion engines, it is also possible to increase or regulate the amount of available reducing agent by means of so-called engine parameter tuning. This can be done by e.g. fuel injection timing, valve timing, post-injection, control of charging pressure and/or fuel injection pressure, EGR, transmission ratio, etc.

Advantageously, the additional amount 19, 19', 19" of reducing agent (HC) can be regulated on the basis of a measured or previously mapped content 20 of reducing agent (HC) and/or nitrogen oxides (NO_x) in the exhaust gases 12, 12'.

The measured content 20 of reducing agent (HC) or nitrogen oxides (NO_x) in the catalytically converted exhaust gases (12') can also be used in a diagnostic control system 22, providing an indication of the status of the catalytic conversion.

The exhaust gases 12 can also be passed through a device having the ability to store and when necessary release nitrogen oxides (NO_x) before the

oxidation over the oxidation catalyst (OX), according to the first reaction 3. Such NO_x-absorbers are well-known to the person skilled in the art, and will not be described in any greater detail herein. Before the oxidation, the exhaust gases 12 can also be passed through a previously known device having the ability to store, and when necessary release, reducing agent (HC), e.g. hydrocarbon. This embodiment is useful for e.g. cold starts of an internal combustion engine.

In order to ensure that the oxidation catalyst (OX) and/or the reduction catalyst (RED) is functioning in the best possible way, i.e. are within an active temperature interval, the temperature of the exhaust gases can be regulated before the passage through the porous material 21 according to the invention. This can be done with any previously known device 23 which is suitable for the purpose.

In order to further improve the catalytic conversion, the exhaust gases can be allowed to pass a second oxidation catalyst 24, over which oxidation of residues of reducing agent and/or carbon monoxide can take place. In this way, it is ensured that the exhaust gases, which have been at least partially catalytically converted over the porous material 21, reach a sufficiently high degree of catalytic conversion.

It is advantageous for the method of the invention if the exhaust gases 12 originate from an internal combustion engine 25, and the reducing agent (HC) comprises a hydrocarbon (H_xC_y) and/or a chemical compound ($H_xC_yO_zS_w$) further comprising oxygen and/or sulphur.

Furthermore, the fuel 26 consumption of the internal combustion engine 25 will influence the chemical composition of the exhaust gases 12. Legislative regulations are imposed both on fuel consumption and the residue content of nitrogen oxides (NO_x) in the catalytically converted exhaust gases 12'. In one embodiment of the invention, both the fuel consumption of the internal

combustion engine, and the residue content of nitrogen oxides (NO_x) in the catalytically converted exhaust gases 12', are regulated in order to fulfil the relevant legislative regulations. .

In one preferred embodiment of the method according to the invention, the internal combustion engine 25 is a diesel engine and the reducing agent (HC) originates from internal combustion in said diesel engine.

When diesel engines are concerned, an additional amount 19 of reducing agent (HC) can advantageously be supplied to the engine via a fuel injector of the diesel engine and/or via a separate injector for additional reducing agent.

It is preferred to use a porous material according to the invention, for catalytic conversion of exhaust gases 12, which have an oxygen surplus and, accordingly, are difficult to convert in conventional catalytic converters, e.g. three-way converters. In such use, the porous material provides functions both for the oxidation of nitrogen monoxide (NO) into nitrogen dioxide (NO_2) and for the reduction of nitrogen dioxide (NO_2) into nitrogen (N_2).

It is also preferred with an arrangement 27, according to the invention, for catalytic conversion of exhaust gases which originate from an internal combustion engine 25. Thereby, the arrangement comprises a porous material 21 according to the invention or, furthermore, operates through a method according to the invention.

According to yet another embodiment of the porous material according to the invention, the first porous structure 2, 2' on an average exhibits smaller entrances 7 for the reducing agent (HC) than the second porous structure 5, 5'. In this way, the reducing agent (HC) is prevented from getting into contact with the oxidation catalyst (OX), enclosed inside the first porous structure 2, 2', but is not prevented from coming into contact with the reduction catalyst (RED) in

the second porous structure 5, 5'. The pores in the first porous structure 2, 2' should preferably primarily have an effective size of 3-4.5Å?

Thus, the oxidation catalyst (OX) enclosed inside the first porous structure 2, 2', may have such dimensions that the reducing agent (HC) 4, 4' is sterically prevented from coming into contact with the oxidation catalyst (OX). In this context, the term "first porous structure" primarily refers to internal micro-pores in the carrier material or micro-pores between carrier particles or grains.

Even in the case of using the above mentioned pores with a smaller entrance, the use of iron (Fe) and silver (Ag) surprisingly enhances the desired conversion of NO_x to N_2.

Examples:

Below will be presented a number of examples of possible materials as well as the result of a test which compares the iron/silver combination according to the invention with a previously known platinum based catalyst.

MFI:

free diameter:

10 rings 5.1 x 5.5 Å

10 rings 5.3 x 5.6 Å

MOR:

free diameter:

12 rings 6.5 x 7,0 Å

8 rings 2.6 x 5.7 Å

<u>Evaluation of catalytic conversion efficiency</u>

In order to describe the improved conversion of exhaust gases at the present invention compared to previously known catalysts, the result of a test which

compares the iron/silver combination according to the invention with a previously known platinum based catalyst will be described below, and the results is presented in table 1.

The test is performed on two catalysts which differ only in the use of different catalytic active material in the oxidation catalyst part of the catalyst. The first catalyst is a dual pore size catalyst according to WO 99/29400 (DP-Pt) with an oxidation catalyst pore treated with platinum, the second catalyst is a catalyst according to the invention with an oxidation catalyst pore treated with iron and silver.

Table 1 lists temperatures at which the conversion of NO to N_2 was obtained and graph 1 shows the results graphically.

The test will show the performance of a Fe-MFI zeolite by adding silver. A further gain in NOx conversion is obtained by adding mordenite zeolite.

Before the evaluation, the obtained Ag-Fe-MFI and H-MOR, and physical mixtures of these, were compressed into pellets, i.e. model porous samples, and the catalytic conversion efficiency of the different porous samples was evaluated.

In the prepared porous samples, the Ag-Fe-MFI were intended to provide the earlier-mentioned NO-oxidation function, whereas the H-MOR were intended to provide the earlier-mentioned NO_2-reduction function.
The results of the test with decane, HC/NOx = 3 is presented in table 1:

Table 1

catalyst	DP-Pt catalyst	invention

NO to N2 conversion	26.5	48.4
NO to N2O formation	13.6	0.2

According to the test the present invention enhances the degree of conversion from 26 % to 48 % compared to the DP-Pt catalyst, when using the same test conditions.

The present invention is not restricted to the described embodiments, but may be altered within the scope of the claims.

CLAIMS

1. Porous material for catalytic conversion of exhaust gases, said porous material (1) comprising a carrier with a first porous structure (2, 2'), and an oxidation catalyst (OX) which in the presence of oxygen (O_2), according to a first reaction (3), has the ability to catalyse oxidation of nitrogen monoxide (NO) into nitrogen dioxide (NO_2) and, according to a second reaction (4, 4'), to catalyse oxidation of a reducing agent (HC), which oxidation catalyst (OX) is enclosed inside the first porous structure (2, 2'), c h a r a c t e r i z e d i n that the oxidation catalyst (OX) comprises iron (Fe) and silver (Ag) loaded on a zeolite.

2. Porous material for catalytic conversion of exhaust gases according to claim 1, c h a r a c t e r i z e d i n that the first porous structure (2, 2') comprises a zeolite with MFI framework structure type.

3. Porous material for catalytic conversion of exhaust gases according to claim 2, c h a r a c t e r i z e d i n that the oxidation catalyst (OX), due to the iron (Fe) and silver (Ag), is arranged to prevent the reducing agent (HC) from reacting in the oxidation catalyst (OX) or arranged to slow down the reaction of the reducing agent (HC) in the oxidation catalyst (OX), in order to enable primarily the first reaction (3), out of said first and second reactions, to take place over the oxidation catalyst (OX) during the catalytic conversion of the exhaust gases.

4. Porous material for catalytic conversion of exhaust gases according to claim 1, said porous material (1) further comprising a carrier with a second porous structure (5, 5') and a reduction catalyst (RED), which in the presence of the reducing agent (HC) is able to selectively catalyse reduction of nitrogen dioxide (NO_2) into nitrogen (N_2), according to a third reaction (6), whereby the reducing agent (HC) participates in the third reaction (6) and is at least partially consumed, c h a r a c t e r i z e d i n that the reduction catalyst (RED) is

located in the second porous structure (5, 5'), which has such dimensions that the reducing agent (HC) can come into contact with the reduction catalyst (RED) in order to enable the third reaction (6) to take place.

5. Porous material for catalytic conversion of exhaust gases according to claim 4, characterized in that the first porous structure (2, 2') on an average exhibits smaller entrances (7) for the reducing agent (HC) than the second porous structure (5, 5').

6. Porous material for catalytic conversion of exhaust gases according to any of claims 4 -5, characterized in that both the first (2, 2') and the second (5, 5') porous structures are provided in the same layer/coating of the porous material.

7. Porous material for catalytic conversion of exhaust gases according to any of claims 4 -5, characterized in that the first (2, 2') and the second porous structures (5, 5') are provided in different layers/coatings of the porous material.

8. Porous material for catalytic conversion of exhaust gases according to any one of claims 4-7, characterized in that the carrier with the second porous structure (5, 5') has been adapted to molecule size and/or adsorption properties of the reducing agent (HC).

9. Porous material for catalytic conversion of exhaust gases according to any one of claims 4-8, characterized in that the ratio between oxidation catalyst (OX) and reduction catalyst (RED) has been optimized so that the production of nitrogen dioxide (NO_2), according to the first reaction (3), essentially corresponds to the consumption of nitrogen dioxide (NO_2), according to the third reaction (6).

10. Porous material for catalytic conversion of exhaust gases according to any one of claims 4-9, further comprising a first portion (10) and a second portion (11), wherein the first portion (10) is intended to receive the exhaust gases (12) before the second portion (11) during the catalytic conversion, characterized in that the first portion (10) contains a larger quantity of the oxidation catalyst (OX) than the second portion (11), whereas the second portion (11) contains a larger quantity of the reduction catalyst (RED) than the first portion (10).

11. Porous material for catalytic conversion of exhaust gases according to claim 10, characterized in that the porous material comprises a second zeolite (15), providing the second porous structure (5, 5').

12. Porous material for catalytic conversion of exhaust gases according to claim 11, characterized in that the porous material comprises a physical mixture (13) of the first zeolite (14) and the second zeolite (15).

13. Porous material for catalytic conversion of exhaust gases according to claim 12, characterized in that the porous material comprises a layered structure (16, 17) of the first zeolite (14) and the second zeolite (15), wherein said first and second zeolites (14, 15), depending on the expected composition of the exhaust gases (12) which are to be catalytically converted, have been arranged in relation to each other in said layered structure (16, 17), preferably so that the second zeolite (15) will encounter the exhaust gases (12) before the first zeolite (14) during the catalytic conversion.

14. Porous material for catalytic conversion of exhaust gases according to claim 12, characterized in that the second zeolite, providing the second porous structure (5, 5'), has been applied by over-growth onto the first zeolite, providing the first porous structure (2, 2').

15. Porous material for catalytic conversion of exhaust gases according to anyone of claims 12-14, c h a r a c t e r i z e d i n that the content of oxidation catalyst (OX) has been reduced in outer layers (8) of the first zeolite by means of regulating penetration depth and/or dispersion.

16. Porous material for catalytic conversion of exhaust gases according to any one of claims 12-15, c h a r a c t e r i z e d i n that an additional zeolite crystal layer with a reduced content of oxidation catalyst (OX) has been crystallized onto the crystal structure of the first zeolite.

17. Porous material for catalytic conversion of exhaust gases according to any one of claims 12-16, c h a r a c t e r i z e d i n that the crystal structure of the first zeolite comprises crystal grains having a grain size (9) and a shape which has been optimized both in order to prevent reaction of the reducing agent (HC), and in order to allow effective oxidation of NO to NO_2.

18. Porous material for catalytic conversion of exhaust gases according to any one of claims 4-16, c h a r a c t e r i z e d i n that the reducing agent (HC), which is at least partially consumed according to the third reaction (6), is a hydrocarbon (H_xC_y) and/or a chemical compound ($H_xC_yO_zS_w$) further comprising oxygen/and or sulphur.

19. Porous material for catalytic conversion of exhaust gases according to any one of claims 2-20, c h a r a c t e r i z e d i n that the reduction catalyst is an acidic zeolite catalyst.

20. Porous material for catalytic conversion of exhaust gases according to any one of claims 2-21, c h a r a c t e r i z e d i n that the reduction catalyst (RED) comprises Brönstedt acid sites, silver (Ag), iron (Fe) copper (Cu), Rhodium (Rh), Indium (In), Iridium (Ir), or combinations of these.

21. Porous material for catalytic conversion of exhaust gases according to any one of the preceding claims, c h a r a c t e r i z e d i n that the first or/and the second porous structure is/are provided in carriers attached to a substrate (18).

22. Method for catalytic conversion of exhaust gases, comprising oxidation of nitrogen monoxide (NO) into nitrogen dioxide (NO_2) over an oxidation catalyst (OX), according to a first reaction (3), whereby said oxidation catalyst (OX) also has the ability to, according to a second reaction (4, 4'), catalyse oxidation of a reducing agent (HC), c h a r a c t e r i z e d i n that the reducing agent (HC) (4, 4') is prevented from coming into contact with the oxidation catalyst (OX) or that the reaction of the reducing agent (HC) in the oxidation catalyst (OX) is slowed down, as a result of which primarily the first reaction (3), out of said first and second reactions, takes place over the oxidation catalyst (OX), due to the presence of iron (Fe) and silver (Ag).

23. Method for catalytic conversion of exhaust gases according to claim 22, further comprising a third reaction (6) over a reduction catalyst (RED), wherein nitrogen dioxide (NO_2), in the presence of a reducing agent (HC), is reduced into nitrogen (N_2), c h a r a c t e r i z e d i n that the reducing agent (HC) participates in the third reaction (6) and thereby is at least partially consumed, in order to provide catalytically converted exhaust gases (12') having a reduced content of nitrogen monoxide (NO), nitrogen dioxide (NO_2) and the reducing agent (HC), and a proportionately low content of dinitrogen oxide (N_2O) and/or carbon monoxide (CO).

24. Method for catalytic conversion of exhaust gases according to claim 22-23, c h a r a c t e r i z e d i n that an additional amount (19, 19', 19") of reducing agent (HC) is added before reduction takes place over the reduction catalyst (RED), according to the third reaction (6).

25. Method for catalytic conversion of exhaust gases according to claim 24,

characterized in that the additional amount (19, 19', 19") of reducing agent (HC) is regulated on the basis of a measured or previously mapped content (20) of reducing agent (HC) and/or nitrogen oxides (NO_x) in the exhaust gases (12, 12').

26. Method for catalytic conversion of exhaust gases according to claim 24, characterized in that the measured content (20) of reducing agent (HC) or nitrogen oxides (NO_x) in the catalytically converted exhaust gases (12') is used in a diagnostic control system (22) as a measure of the status of the catalytic conversion.

27. Method for catalytic conversion of exhaust gases according to any one of claims 22-26, characterized in that the exhaust gases (12), before oxidation over the oxidation catalyst (OX) according to the first reaction (3), are passed through a device having the ability to store and when necessary release nitrogen oxides (NO_x).

28. Method for catalytic conversion of exhaust gases according to any one of claims 22-27, characterized in that the exhaust gases (12), before oxidation over the oxidation catalyst (OX) according to the first reaction (3), are passed through a device having the ability to store and when necessary release reducing agent (HC).

29. Method for catalytic conversion of exhaust gases according to any one of claims22-28, characterized in that the temperature of the exhaust gases is regulated (23) in order to be within an active temperature interval of the oxidation catalyst (OX) and/or the reduction catalyst (RED).

30. Method for catalytic conversion of exhaust gases according to any one of claims 22-29, characterized in that the at least partially catalytically converted exhaust gases, after (21) oxidation over the oxidation catalyst (OX) and reduction over the reduction catalyst (RED), are allowed to pass a second

oxidation catalyst (24) over which oxidation of residues of reducing agent (HC) and/or carbon monoxide can take place.

31. Method for catalytic conversion of exhaust gases according to any one of claims 22-30, c h a r a c t e r i z e d i n that the exhaust gases (12) originate from an internal combustion engine (25), and that the reducing agent (HC) comprises a hydrocarbon (H_xC_y) and/or a chemical compound ($H_xC_yO_zS_w$) further containing oxygen/and or sulphur.

32. Method for catalytic conversion of exhaust gases according to claim 31, c h a r a c t e r i z e d i n that both the fuel (26) consumption of the internal combustion engine (25), influencing the chemical composition of the exhaust gases (12), and the residue content of nitrogen oxides (NO_x) in the catalytically converted exhaust gases (12') are regulated in order to fulfil relevant legislative regulations.

33. Method for catalytic conversion of exhaust gases according to claim 31 or 32, c h a r a c t e r i z e d i n that the internal combustion engine (25) is a diesel engine and that the reducing agent (HC) originates from internal combustion in said diesel engine.

34. Method for catalytic conversion of exhaust gases according to claim 33, c h a r a c t e r i z e d i n that an additional amount (19) of reducing agent (HC) is added via a fuel injector of the diesel engine and/or via a separate injector for additional reducing agent.

35. Use of a porous material, according to any one of claims 2-21, providing functions both for the oxidation of nitrogen monoxide (NO) into nitrogen dioxide (NO_2) and for the reduction of nitrogen dioxide (NO_2) into nitrogen (N_2), for catalytic conversion of exhaust gases (12) which have an oxygen surplus.

36. Catalytic conversion device (10, 11) for exhaust gases,

c h a r a c t e r i z e d i n that the catalytic conversion device (10, 11) comprises a porous material (1) according to any one of claims 1-21.

37. Arrangement for catalytic conversion of exhaust gases, whereby said exhaust gases (12) originate from an internal combustion engine (25), c h a r a c t e r i z e d i n that the arrangement comprises a porous material (1) according to any one of claims 1-21.

38. Arrangement for catalytic conversion of exhaust gases according to claim 37, c h a r a c t e r i z e d i n that the arrangement operates through a method according to any one of claims 22-34.

ABSTRACT

The invention refers to a porous material (1) for catalytic conversion of exhaust gases. Said porous material comprises a carrier with a first porous structure (2, 2'), and an oxidation catalyst (OX) which in the presence of oxygen (O_2), according to a first reaction (3), has the ability to catalyse oxidation of nitrogen monoxide (NO) into nitrogen dioxide (NO_2) and, according to a second reaction (4, 4'), to catalyse oxidation of a reducing agent (HC), which oxidation catalyst (OX) is enclosed inside the first porous structure (2, 2'). The invention is characterised in that the oxidation catalyst (OX) comprises iron (Fe) and silver (Ag) loaded on a zeolite. The invention also relates to a method and an arrangement and a catalytic conversion device which utilize the porous material, and indicates an advantageous use of the porous material.

(Fig. 1)

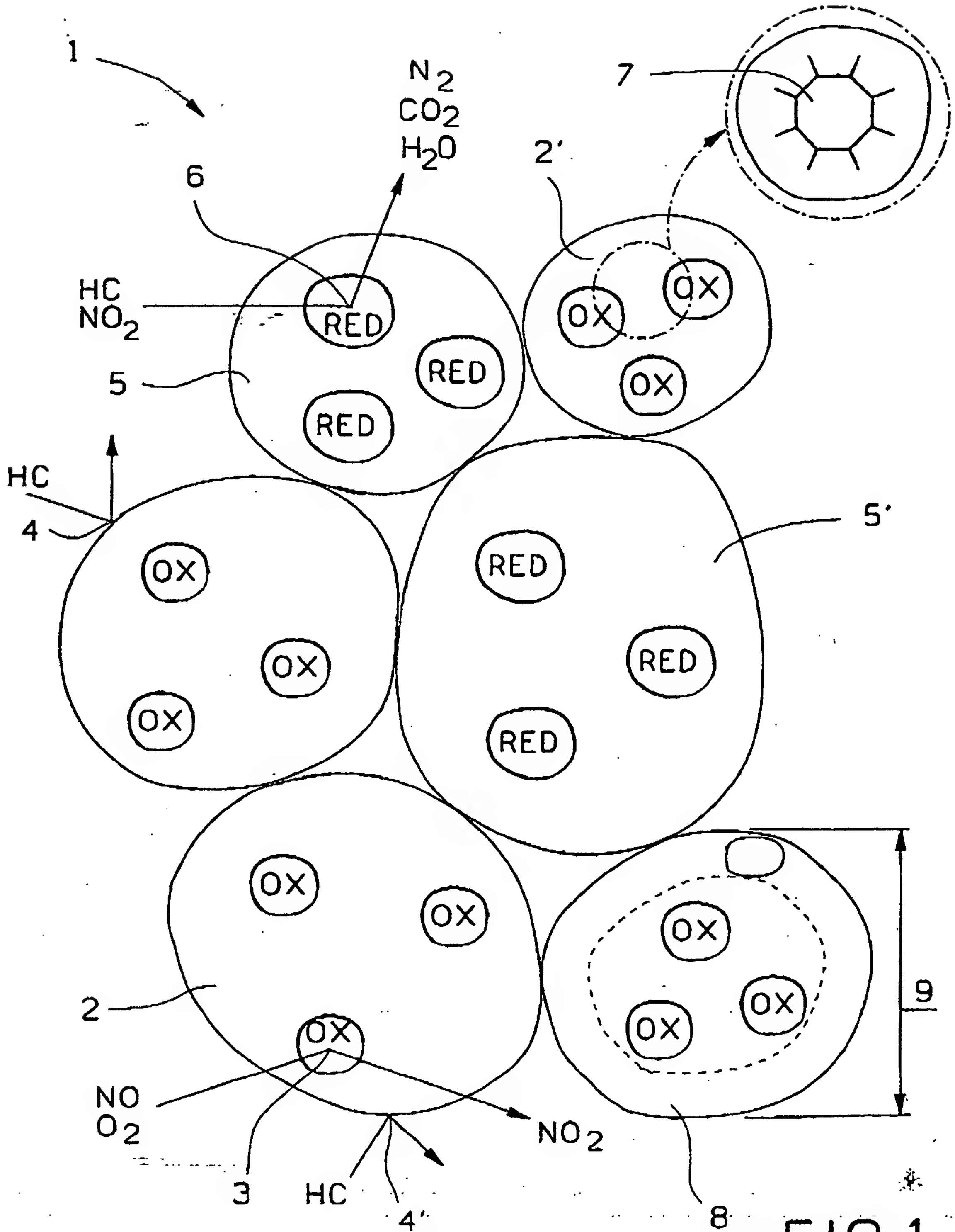
1
N 2
CO2
H2O
6
7
2'
HC
NO2
RED
RED
RED
OX
OX
OX
5
HC
4
OX
OX
OX
RED
RED
RED
5'
OX
OX
OX
OX
OX
OX
OX
2
9
NO
O2
NO2
3
HC
4'
8

FIG.1

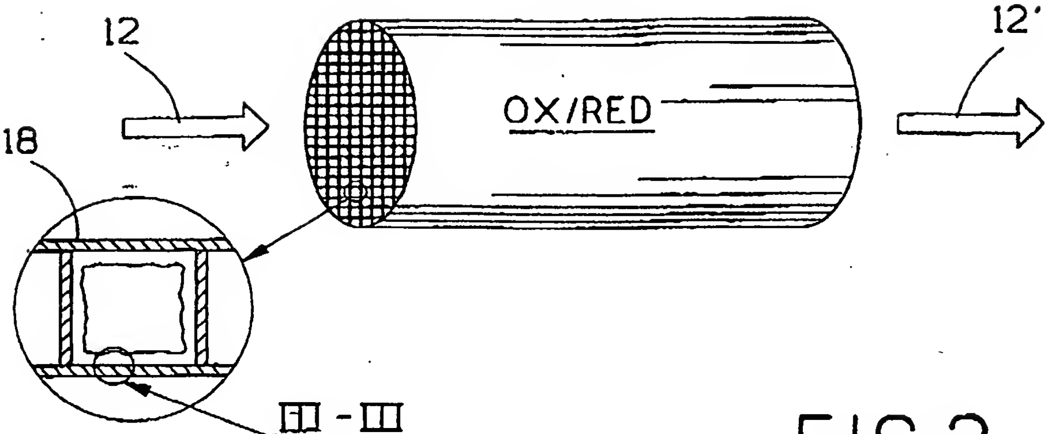

FIG.2

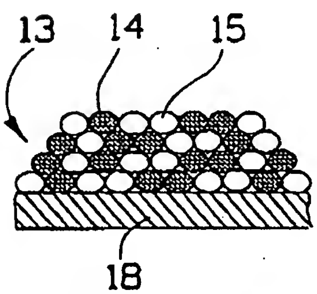

FIG.3A

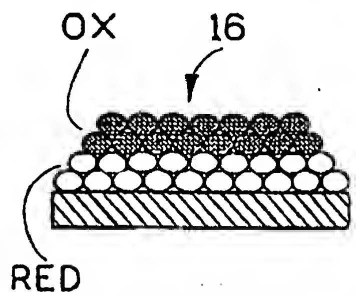

FIG.3B

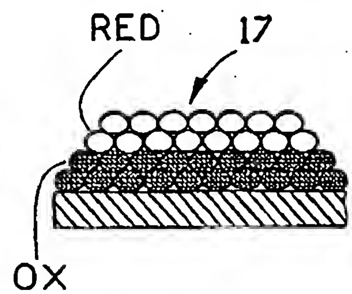

FIG.3C

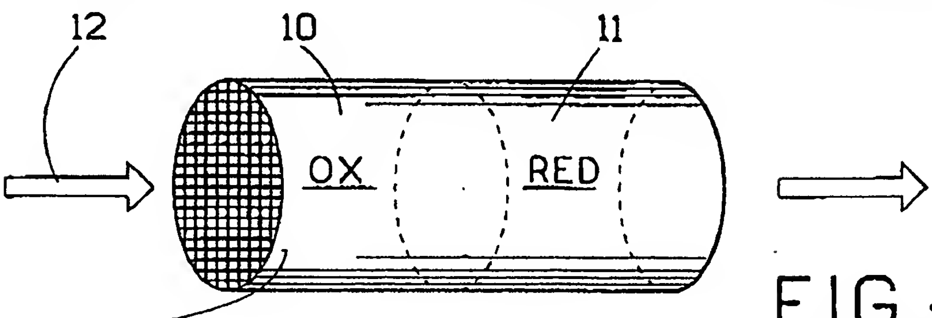

FIG.4A

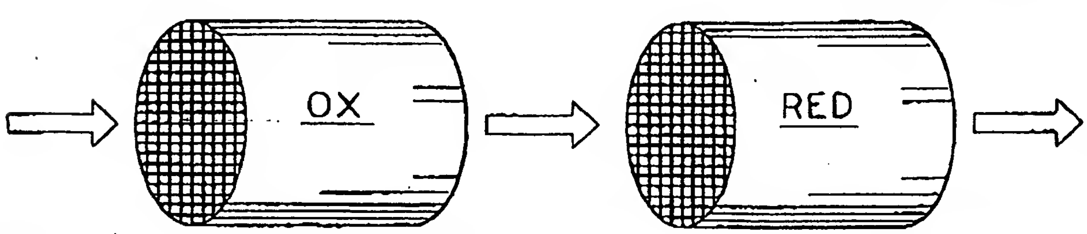

FIG.4B

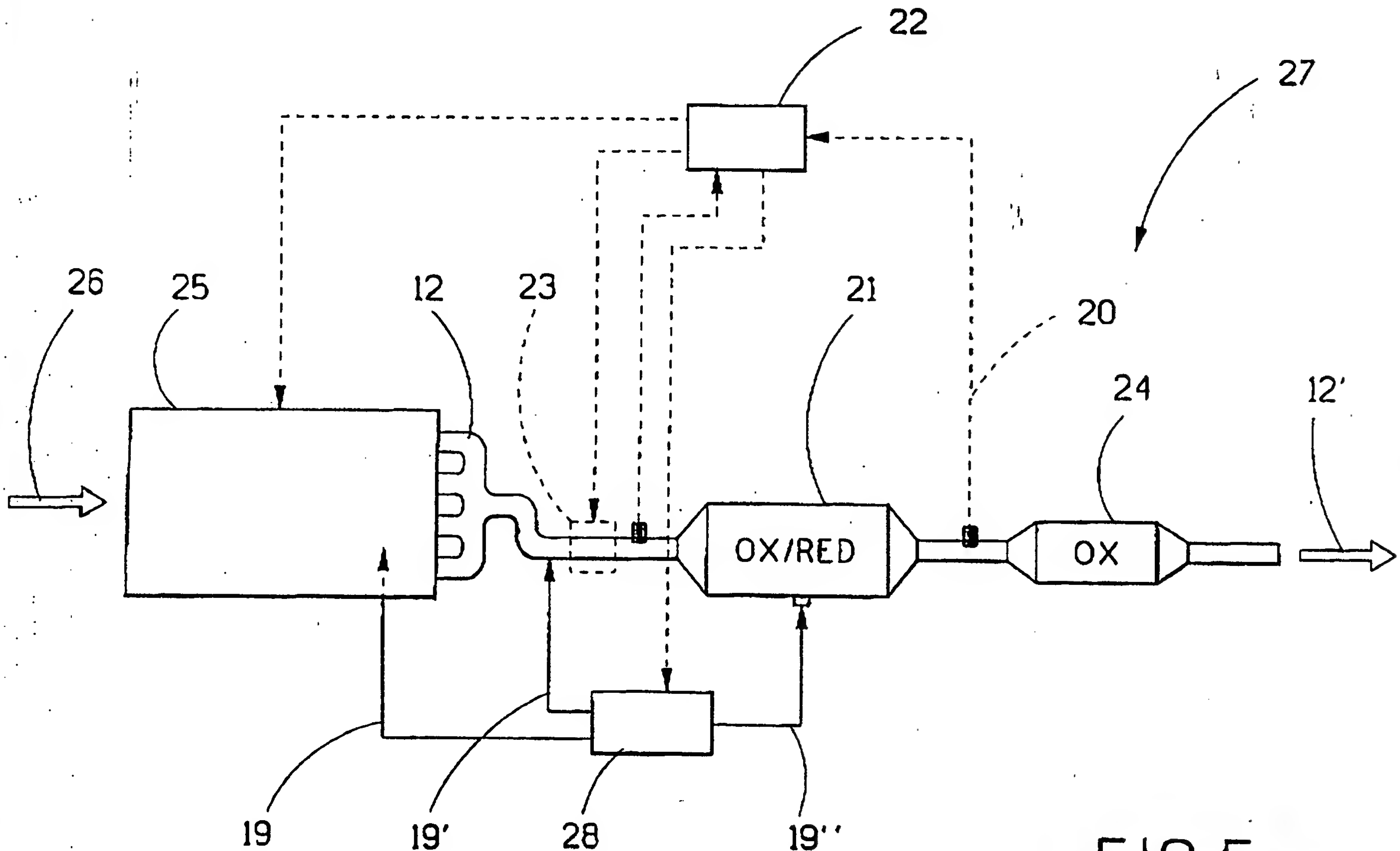

FIG.5